SHORT PAPER

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Hypervalent iodine in synthesis 58: synthesis of aryl esters of dithiocarbamic acids using polymeric diaryliodonium salts[†]

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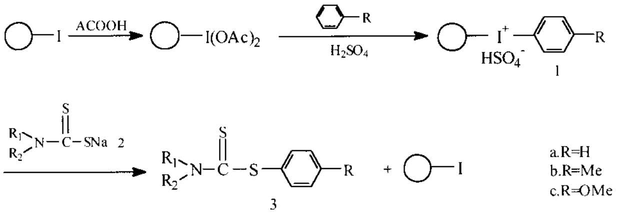
Polymer-supported diaryliodonium salts were prepared and employed as aryl transfer reagents for the synthesis of aryl esters of dithiocarbamic acids.

The advantages of polymer-supported reactive species are now widely recognised by organic chemists, and the exploitation of these systems is developing both in academic and industrial laboratories.[1] However, in spite of the ready availability of numerous polymer-supported reagents, none of them serves as aryl cation equivalent that performs the arylation of nucleophilic species. Recently, our interest in electrophilic arylation by diaryliodonium salts[2] and polymer supported synthesis[3] has led to the development of polymer-supported diaryliodonium salts, the polymeric reagents acting as efficient sources of aryl cations. In this communication, we describe their preparation and synthetic power in the arylation of dithiocarbamates.[4]

For the preparation of diaryliodonium salts, a general method involves the reaction of phenyliodine diacetate (PID) with arenes in acidic condition.[5] On the basis of this, a practical approach to polymeric diaryliodonium salts might be provided. We first prepared polymer-supported phenyliodine diacetate (PPID) from commercially available polystyrene ($\bar{M}_w$ 250 000) by our previously reported method.[3] The prepared PPID was then treated with arenes in the presence of sulfuric acid to obtain polymer-supported diaryliodonium salts (Scheme 1). The conversion was proved to be successful by IR characterization of the resulting resin. Accompanying the rough disappearance of the characteristic peaks of PPID at 1645cm^{-1} (C=O) and 1290cm^{-1} (I–O–C), peaks at 3450cm^{-1} (O–H), 1180cm^{-1} (SO_2) and 1040cm^{-1} (S–O) emerged indicating the presence of bisulfate counter anion. To determine the exact capacity of functional groups, the prepared resin was submitted to EA analysis (S). The results were acceptable (**1a** 1.39mmol/g; **1b** 1.53mmol/g; **1c** 1.47mmol/g), qualifying the prepared resins as practical polymeric reagents.

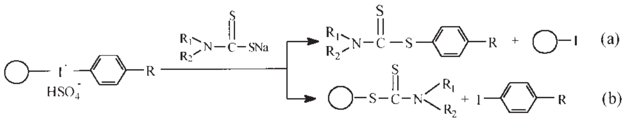


Scheme 1

In contrast to another method solely suitable for the reaction with arenes bearing alkoxyl groups,[4b] this procedure was applicable to both nonsubstitued arenes and arenes with alkoxyl or alkyl groups. However, satisfactory results were not found in attempts to prepare polymeric diaryliodonium salts with electron deficient arenes attached to the iodonium moiety. This was reasonable considering that the conversion of PPID into polymeric diaryliodonium salts was promoted by the nucleophilicity of corresponding arenes.

As depicted in Scheme 1, the prepared polymer-supported diaryliodonium salts were employed to effect the arylation of dithiocarbamates. The desired aryl esters of dithiocarbamic acids are of considerable interest because of their antimicrobial activity[6] and synthetic application.[6,7] We have reported an effective method for the preparation of them with diaryliodonium salts,[2b] which is superior to the previous ones.[7,8] For further improvement, immobilization of diaryliodonium salts on polymer supports offers ease of work-up.

The recently developed liquid-phase methodology emphasizes the solubility of linear polymer supports.[9] In optimising our reaction condition, we found that DMF appeared to be the desirable solvent for the homogeneous purpose. As a result, the polymer-supported diaryliodonium salts readily reacted with sodium dithiocarbamates in DMF at 60–70°C to afford aryl esters of dithiocarbamic acids in moderate yields (Table 1).



Scheme 2

Theoretically, two pathways were possible in our reaction due to the unsymmetrical nature of polymeric diaryliodonium salts (Scheme 2). Herein, the selectivity of polymeric diaryliodonium salts was predominantly preferential to our desired route (a), while only trace amount of iodoarenes were detected in occasional cases. We might attribute this favorable selectivity to factors such as the bulky macromolecule chain, the soft nucleophiles, and the homogeneous reaction conditions.

In summary, we have examined the synthetic utility of polymeric diaryliodonium salts and achieved the arylation of dithiocarbamates. The reaction offered a convenient isolation

Table 1 Synthesis of aryl esters of dithiocarbamic acids 3

Entry	R_1	R_2	Polymer	m.p.(lit)°C	Time (h)	Yield[a] %
1	CH_3	CH_3	**1a**	92–94(94–95)[8c]	8	51
2	C_2H_5	C_2H_5	**1a**	43–45(46)[8c]	12	42
3	$–(CH_2)_5–$	/	**1a**	114–116(116–117)[8c]	12	47
4	Ph	H	**1a**	153(148–150)[2b]	10	39
5	CH_3	CH_3	**1b**	111–112(111–112)[8c]	12	72
6	C_2H_5	C_2H_5	**1b**	75–76(77–78)[8c]	14	63
7	$–(CH_2)_5–$	/	**1b**	117–119(118–119)[8c]	12	67
8	CH_3	CH_3	**1c**	95(92–93)[2b]	12	54
9	$–(CH_2)_5–$	/	**1c**	101–102(102–103)[8a]	12	48

[a] Products were characterised by ^{1}H-NMR, IR which were consistent with the literature data.[2b]

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

procedure and moderate yield. Further investigation of the reactivity of these polymeric reagents using palladium as catalyst will be reported in due course.

Experimental

IR spectra were recorded on a PE-683 Spectrophotometer. ^{1}H-NMR spectra were recorded on a PMX-60 Spectrometer, using CCl_4 as the solvent with TMS as an internal standard. Elemental analyses were carried out on a EA 1110 instrument. All melting points are uncorrected.

Preparation of polymer-supported diaryliodonium salts: To a mixture of PPID (3.0 g), arene (30 mol) in acetic acid (200 ml), conc. sulfuric acid (30 ml) was added dropwise with stirring. The resulting mixture was usually homogeneous except for the preparation of **1a**. The stirring was continued for about 60h, 20h, 20h for **1a**, **1b**, **1c** respectively at room temperature. Water was added to precipitate the reacted polymer. The resulting resin was filtered and washed with ether. The dried resin weighed 3.2–3.4g.

1a dark yellow. IR (KBr): 3450, 1484, 1445, 1408, 1168, 1040, 1005, 820, 740, 680 cm^{-1}. E.A.: S 4.35%

1b pale yellow. IR (KBr): 3450, 1484, 1445, 1408, 1180, 1070, 1005, 820cm^{-1}. E.A.: S 4.58%

1c pale brown IR (KBr): 3450, 1570, 1487, 1408, 1255, 1175, 1030, 1005, 820m^{-1}. E.A.: S 4.89%

Typical procedure for the synthesis of phenyl esters of N,N-dimethyl dithiocarbanic acid: To a suspension of polymeric diaryliodonium salt **1a** (1 mmol) in DMF (10 ml), sodium N,N-dimethyl dithiocarbamic acid (1.2 mmol) was added and the mixture was stirred an 60–70°C. As the reaction proceeded, the resin was dissolved and the mixture turned to a homogenous solution. The progress of the reaction was monitored by TLC. When the reaction was complete as the spot of product no longer enlarged, water (5 ml) was added to precipitate the polymer species. After filtration, the filtrate was extracted with ether (8 ml × 3), dried with $MgSO_4$ and evaporated *in vacuo* to afford the crude product. Pure product was obtained by plate chromatography (petroleum ether/EtOAc=6:1) as pale yellow solid (102 mg). m.p.92–94°C (lit.[8c] 94–95°C). IR (KBr): 2940, 1508, 1385, 1260, 1150, 990, 870, 690, 570cm^{-1}. ^{1}H-NMR δ:3.55(s,6H), 7.55(s,5H).

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References and notes

1 (a) D.C. Bailey and S.H. Langer, *Chem. Rev*., 1981, **81**, 109; (b) A.Akelah and D.C. Sherrington, *Chem. Rev.*, 1981, **81**, 557; (c) P. Laszlo; (Ed). *Preparative Chemistry Using Polymer-Supported Reagents, Academic, San Diego*, 1987**;** (d) P. Hodge and D.C. Sherrington, *Polymer-Supported Reaction in Synthesis,* Wiley, New York, 1990; (e) S.J. Shuttlewurth, S.M. Allin and P.K. Sharma, *Synthesis*, 1997, 1217.

2 (a) Z.C. Chen, Y.Y. Jin and P.J. Stang, *J. Org. Chem*., 1987, **52**, 4115; (b) Z.C. Chen, Y.Y. Jin and P.J. Stang, *J. Org. Chem*., 1987**, 52**, 4117; (c) Z.C. Chen, Y.Y. Jin and R.Y. Yang, *Synthesis*, 1988, 723; (d) J.Z. You and Z.C. Chen, *Synthesis*, 1992, 521; (e) J.Z. You and Z.C. Chen, *Synth. Commun.*, 1992, **22**, 1441; (f) J.Z. You and Z.C. Chen, *Synthesis,* 1992**,** 633; (g) Z.D. Liu, D.W. Chen and Z.C. Chen, *Synth. Commun.*, 1992, **22**, 2903; (h) Z.D. Liu and Z.C. Chen. *Synthesis*, 1993, 373; (i) Z.D. Liu and Z.C. Chen, *Synth. Commun.*, 1993, **23**, 2675; (j) Z.D. Liu, H. Zeng and Z.C. Chen, *Synth. Commun*., 1994, **24**, 475; (k) M. Xia and Z.C. Chen, *Synth. Commun*., 1997, **27**, 1309.

3 G.P. Wang and Z.C. Chen, *Synth. Commun*., 1999, **29**, 2859.

4 Although the preparation of polymeric diaryliodonium salts has been occasionally reported, their application was limited to initiation of polymerization. For relevant references, see: (a) Y.Yamada and M. Okawara. *Makromol. Chem*., 1972, **152**, 153; (b) J.V. Crivello and J.L. Lee, *Polym. Bull*., 1986, **16**, 243; (c) V. Haack and Klemn, *Polym. Bull*., 1994, **33**, 289.

5 T. Kitamura, *et al. Synthesis* 1992, 945.

6 E.E. Reid, *Organic Chemistry of Bivalent Sulfur,* Chemical Publishing: New York, 1982; Vol.IV.

7 K. Jen and M.P. Cava, *Tetrahedron Lett*. 1982, **23**, 2001.

8 (a) N.Teruhisa. *et al., Yakugaku Zasshi* 1968, **88**(2), 227; (b) W. Will, *Ber. Dtsh. Chem. Ges*. 1982, **15**, 1303; (c) A.M. Clifford and J.G. Lichty, *J. Am. Chem. Soc*., 1932, **54**,1163; (d) J.R. Grunwell. *J. Org. Chem*., 1970, **35**, 1500.

9 D.J. Gravert and K.D, Janda, *Chem. Rev*., 1997, **97**, 489.